11192 J. Phys. Chem. A **2001,** *105,* 11192−11196

The Vibrational Spectrum of Fullerene C_{60}

Vincenzo Schettino,* Marco Pagliai, Lucia Ciabini, and Gianni Cardini

Laboratorio di Spettroscopia Molecolare, Dipartimento di Chimica, Via Gino Capponi 9, 50121 Firenze, Italy, and European Laboratory for Nonlinear Spectroscopy (LENS), Largo E. Fermi 2, 50125 Firenze, Italy

Received: July 25, 2001; In Final Form: September 26, 2001

Using an improved DFT calculation of the vibrational frequencies based on the B3-LYP functional and the 6-31G* basis set, the infrared, Raman, neutron inelastic and luminescence spectra of C_{60} are rediscussed, and a revised assignment of all the silent modes is obtained and compared with the most recent assignments.

Introduction

The vibrational spectra of icosahedral fullerene C_{60} have attracted a considerable attention and have been extensively used as a probe of intra- and intermolecular interactions.[1] The very high symmetry of the C_{60} cluster poses serious problems for a complete identification of the 46 normal modes and of their frequencies. In fact, in the I_h symmetry group, only 14 normal modes are Raman ($2A_g + 8H_g$) or infrared ($4T_{1u}$) active, and these have been assigned with certainty.

The identification of the remaining 32 silent modes ($3T_{1g} + 4T_{2g} + 6G_g + A_u + 5T_{2u} + 6G_u + 7H_u$) has been difficult. Early calculations of the vibrational frequencies of C_{60} based on force field models or on quantum mechanical approaches[1,2] did not display the accuracy required to use them as a reliable guide for a clear-cut identification of the silent modes. Tentative assignments were made from the high-order infrared and Raman spectra.[3−5]

Using the results of the DFT calculation of the vibrational frequencies by Giannozzi and Baroni,[6] Schettino et al.[7] attempted an interpretation of the infrared and Raman spectra of solid C_{60} and proposed an assignment of all the silent modes. Independently, Choi et al.[8] have reported a revised assignment starting again from a DFT calculation. A detailed review of the experimental data on the vibrational spectra of C_{60} has recently been reported by Menéndez and Page,[9] who reconsidered the assignment of all the silent modes relying on DFT calculations by Giannozzi and Baroni[6] and by Adams and Page.[10] We believe that more reliable calculations of the vibrational frequencies are presently feasible. Such calculations are reported in the present paper for C_{60} allowing to obtain a revised assignment of all the vibrational modes.

Computational Details

All the calculations reported in this paper have been carried using the density functional theory. It has been shown[11,12] that using this approach a good agreement with experimental vibrational frequencies can be obtained using an appropriate combination of basis sets and exchange-correlation functionals. Recently, Rauhaut and Pulay[11] and Scott and Radom[12] have shown that one of the best compromises between accuracy and applicability to medium or large size molecules is obtained by the use of the 6-31G* basis set in conjunction with the B3-LYP exchange and correlation functional. This approach, for instance, has been used with considerable success in our laboratory for conjugated or aromatic molecules such as the linear polyenes,[13] retinals,[14] and benzene[15] using a single scaling factor of 0.9613.

Structure minimization and normal frequencies calculation for C_{60} have been carried using the B3-LYP functional and the 6-31G* basis set. The normal frequencies have been calculated using an improved grid in the numerical evaluation of the integrals, after a very-tight optimization of the geometry, using the GAUSSIAN 98 rev. A.7. suite of programs[16] and subsequently have been uniformly scaled by a factor of 0.98. The use of a smaller scaling factor compared to previous calculations[13−15] is justified by the absence in the present case of hydrogen atoms and therefore by the presumably lower anharmonicity of fullerene. Infrared intensities have been obtained using the 6-31G* basis set, while for the Raman intensities, the computer resources available allowed calculations only with the 3-21G basis set.

Results and Discussion

For the assignment of the silent modes of fullerene, one can take advantage of two main circumstances. In the crystal, the intermolecular interactions reduce the local symmetry of the fullerene cage.[17,18] For instance, in the low-temperature phase,[17,18] the site symmetry is S_6. This makes all the silent modes weakly active either in the infrared or in the Raman spectrum. Further, the effect of disorder or crystal imperfections should also be taken into account.[19] As a matter of fact, a wealth of medium and weak bands, besides the free molecule active modes, have been observed in the infrared[20,21] and Raman[3,22] spectra of the crystal. Symmetry reduction has also been found effective in activating silent modes in the spectra of C_{60} adsorbed on various surfaces[23] and in substituted fullerenes.[20,24] Second, in natural fullerene, the $^{12}C_{60}$ and $^{13}C^{12}C_{59}$ species are present in the approximate ratio 5:3. The latter is an isotopic species with only C_s symmetry, and this will likewise give a weak infrared and Raman activity to all the C_{60} silent modes.[19] In connection with this, it should also be noted that in the solid the isotopic species frequencies will generally fall within the density of states of each of the normal modes and will not thus give rise to separate bands. In addition, the inelastic neutron scattering spectra of crystalline C_{60} have been measured[25−27] with appropriate resolution, particularly in the low frequency region, and this can be of great help in localizing the normal modes frequencies independently of their optical activity.

---

* Corresponding author. E-mail: schettin@chim.unifi.it. Fax: +390552476961.

10.1021/jp012874t CCC: $20.00

Taking advantage of all these circumstances and with the help of a normal frequencies calculation[6] based on perturbative density functional theory using pseudopotentials, plane waves basis sets, and numerical methods, a full assignment of the C_{60} normal vibrations has been proposed by two of us and others.[7] Later, few modifications to this assignment have been suggested by Negri et al.[28] Choi et al.,[8] without being apparently aware of our previously proposed assignment[7] nor of the modifications by Negri et al.,[28] have recently rediscussed the full assignment of C_{60} reaching a conclusion that differs from our results[7] in the assignment of 16 modes. These differences include six bands that are only assigned to different symmetry species and 10 modes that differ more substantially. The arguments presented by Choi et al.[8] are essentially based on a DFT calculation of the normal frequencies using the B3-LYP exchange-correlation functional and the 3-21G basis set. Since, as it is known,[11,12] the 3-21G basis set is not able to give the desired accuracy on the vibrational frequencies, Choi et al.[8] were compelled to use a set of scaling factors on the force constants, adjusted for a best fit of the infrared and Raman active fundamentals, obtaining an average difference between calculated and observed frequencies of 8.6 cm^{-1}. In some cases, the scaling factors adopted by Choi et al.[8] are rather large and would lead to a rescaling of the calculated frequencies larger than 5%. We believe that the adopted procedure can in some cases lead to some undesirable errors, as it will be shown in the following, and that a simpler approach can actually be followed. In fact, it has been reported[11,12] that DFT calculations using the B3-LYP functional in conjunction with the more complete 6-31G* basis set, using an uniform scaling factor on the vibrational frequencies, are the best compromise between accuracy and computer resources and produce quite accurate normal frequencies for molecules of moderate size. We have used this same approach to calculate the vibrational frequencies of C_{60}. Using an uniform scaling factor on the frequencies of 0.980, we obtain an average difference between the observed and calculated frequencies of the active A_g, H_g, and T_{1u} modes of only 3.6 cm^{-1}. The present result is a significant improvement compared to that of Choi et al.,[8] who, using more scaling factors, obtained an average discrepancy on the active modes of 6.3 cm^{-1}. We also note in passing that the present calculations are a substantial improvement over the calculations by Giannozzi and Baroni[6] that give an average difference on the active modes of $\sim$15 cm^{-1}. The same considerations apply to the DFT calculations by Adam et al.[10] used by Menéndez and Page.[9] The calculations by Adams et al. [10] give for the infrared and Raman active modes an average discrepancy of $\sim$44 cm^{-1}, mainly concentrated on the high-frequency modes.

The accuracy of the calculations reported in the present paper can also be checked considering the infrared intensities. For the four T_{1u} modes, we obtain, in order of increasing frequencies, relative infrared intensities of 100, 34, 29, and 37. These compare nicely with the experimental values of Chase et al. [24] (100, 32, 26, 34) obtained as product of the peak heights by the bandwidths. Also, the Raman intensities have been calculated but only using the 3-21G basis set. A comparison is in this case more difficult also because the relative Raman intensities strongly depend on the wavelength of the exciting line. In any case, the calculated Raman intensities are in qualitative agreement with Raman experiments with the 488 or 514 nm exciting lines.[22,29,30]

Encouraged by the performance of the present calculation on the active modes, we thought it worthwhile to reconsider the assignment of the silent modes of fullerene using as a guide the B3-LYP/6-31G* calculation. This implies a search of the inactive fundamentals among the weak features of the infrared and Raman spectra of the crystal.

An interpretation of the weak bands appearing in the spectra of crystalline C_{60} has been discussed by Dong et al.[3] with reference to the Raman spectrum and by Wang et al.[5] and Martin et al.[31] with reference to the infrared spectrum. The starting observation of Dong et al.[3] and Wang et al.[5] is that the sharpness of the features appearing in the spectra above 1500 cm^{-1}, which should certainly be assigned as binary combination modes, is a consequence of the small dispersion of the phonon modes and of the weakness of the intermolecular interactions. Thus, in the "almost" ideal C_{60} molecular crystal, the intermolecular interactions should not be very effective in activating the silent modes. The weak spectral features observed in the spectra should therefore be assigned either to combination tones or to silent modes activated by the reduced symmetry of the $^{13}C^{12}C_{59}$ cluster (C_s and not C_{2h}, as reported in ref 5). This conclusion is in contrast with the careful analysis of the low-frequency infrared spectrum of C_{60} reported by Bini et al.,[21] who interpreted the appearance of the u-type silent modes as arising from intermolecular interactions. As a matter of fact, in a molecular dynamics simulation, using a simplified intramolecular force field,[32] Procacci and Berne[33] and Procacci[34] have shown that symmetry reduction and intermolecular interactions in the crystal are very effective in giving a weak infrared intensity to the u-type silent modes. The silent modes can appear in the infrared spectrum with an intensity as large as $\sim 10^{-2}$ times that of the strongest T_{1u} fundamental. Similar effects are expected to occur in the Raman spectrum as well. It is remarkable that in molecular dynamics simulations[34] combination modes are clearly observed in the spectral region above the 1600 cm^{-1} but not much at lower wavenumbers. This suggest that the weak spectral features below 1600 cm^{-1} should be preferentially assigned as silent fundamentals. This is substantiated by calculations carried out in this work on the infrared spectrum of the $^{13}C^{12}C_{59}$ species. It has been found that all the forbidden fundamentals of C_{60} become weakly active in the infrared spectrum. It turns out that the intensity of the activated modes is larger in the neighborhood of the active T_{1u} modes where the mode coupling and the intensity borrowing is larger. It has also been found that the overall infrared intensity of the u-type silent modes is 3 times as large as that of the g-type modes. According to the present calculations in $^{13}C^{12}C_{59}$, the overall infrared intensity of modes inactive in pristine C_{60} is 3.4% that of the T_{1u} derived modes. In Figure 1, the experimental infrared spectrum[21] of crystalline C_{60} below 450 cm^{-1} is compared with the calculated spectrum of $^{13}C^{12}C_{59}$ obtained in this work and with the results of the molecular dynamics simulation by Procacci.[34]

Returning, after these preliminary considerations, to the interpretation of the weak spectral features of C_{60}, the following experimental data were used as a basic reference:

(a) For the Raman spectra, we relied on the single-crystal spectra by Matus and Kuzmany[35] and by van Loosdrecht et al.[22] and on the Raman experiment by Dong et al.[3] These measurements were carried both at room and low temperatures.

(b) For the infrared spectra, we used the spectra of thick C_{60} films reported in previous work by our laboratory.[20,21] The spectra have been remeasured at 8 K. Our infrared spectra are identical with those reported by Martin et al.[4,31] and Wang et al.,[5] except for an improved resolution.

(c) The analysis of the highly structured luminescence spectra from crystalline fullerene exposed to oxygen reported by Nissen

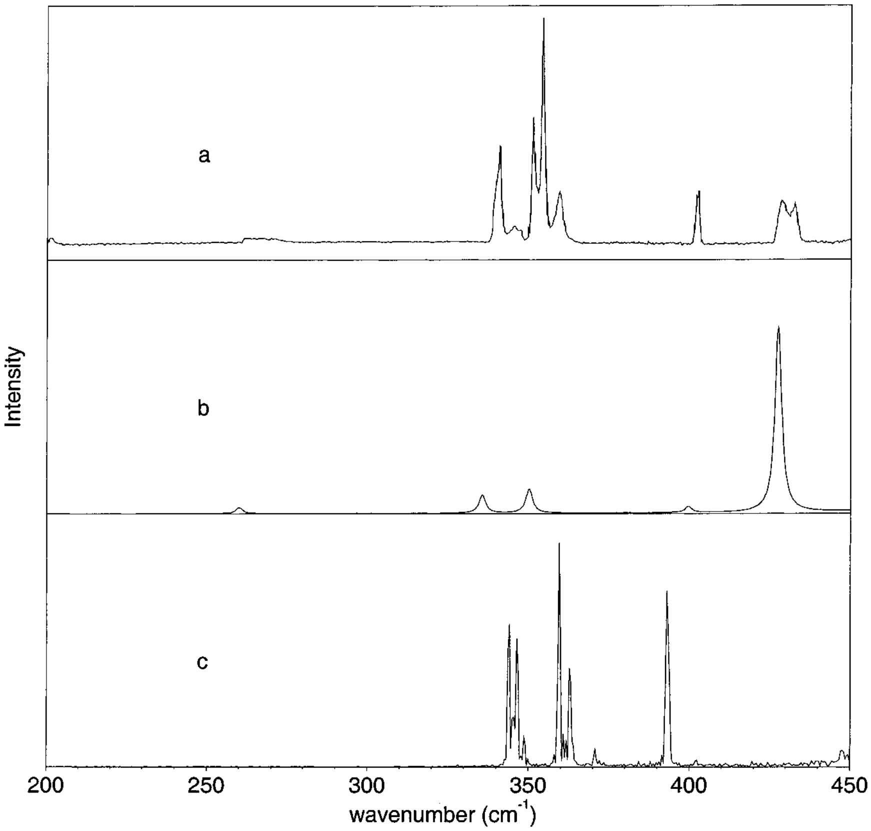

Figure 1. Comparison of the far-infrared spectrum[15] (panel a) with the calculated infrared spectrum of $^{13}C^{12}C_{59}$ (panel b) and with the molecular dynamics simulation of crystalline C_{60} (panel c) obtained in ref 34. The molecular dynamics was carried with a simplified force field (ref 32) and the internal frequencies slightly differ from those of the present work. Intensities are reported in arbitrary units.

et al.[36]
(d) The neutron inelastic scattering spectra already quoted above.[26,27]

The revised assignment resulting from our analysis is summarized in Table 1, where it is compared with our previous results[7] and with the assignments by Choi et al.[8] and by Menéndez and Page.[9] The arguments leading to the new assignment are briefly discussed in the following.

It turns out that it is useful to discuss the spectra region by region, starting from the spectral region below 1000 cm^{-1}. In the 900−1000 cm^{-1} region, three frequencies are calculated corresponding to the A_u, $T_{2u}(3)$, and $G_u(4)$ modes. In nice agreement with calculations, the infrared spectrum exhibits in this region a weak broad band that, at low temperature, shows a clear structure into three components that can be assigned as fundamentals. At least two of these components are observed also in the Raman spectra. Unresolved peaks are present also in the inelastic neutron scattering spectra and in the luminescence spectra. The correspondence between calculations and experiments is surprisingly good also for the 800−900 and 600−700 cm^{-1} regions, where only one normal frequency is calculated ($T_{1g}(2)$ and $H_u(3)$, respectively). Correspondingly, a peak is observed at 823 cm^{-1} in the infrared spectrum with a counterpart in the luminescence and neutron spectra. In the same way, a single very sharp infrared peak is observed in the low-temperature infrared spectrum at 667 cm^{-1}, which has a counterpart in the luminescence and neutron spectra but has not been reported in the Raman spectrum.

The 700−800 cm^{-1} region deserves a particular attention since this is the most congested region of the spectrum. In fact, nine fundamentals are calculated to fall in this region, including two Raman active H_g modes. It is rewarding that this is actually also the most complicated region in the experimental spectra, and a number of peaks develops as a consequence of symmetry reduction, as seen in the infrared spectra of thick samples or in samples adsorbed on surfaces or in substituted fullerenes. To attain an assignment of the region, we chose to identify as fundamentals the three peaks observed in the infrared spectrum on the lower side of the region (including the $H_g(3)$ mode), identifying $H_g(4)$ the sharp infrared peak at 772 cm^{-1} and assigning as u fundamentals the other two prominents peaks in the infrared spectrum and as a g mode the remaining medium intensity peak of the Raman spectrum. In the Supporting Information, the experimental source of the various fundamental frequencies is specified in Table 1S.

The far-infrared spectrum of C_{60} has been discussed in detail,[21] and the assignment is pretty well defined also because there is a consensus from all the available calculations on the fundamental frequencies in this region. The only remaining problem is concerned with the assignment of the 500−600 cm^{-1} region that in the infrared spectrum is dominated by the strong T_{1u} fundamentals. However, closer inspection shows that the lowest of the two T_{1u} fundamentals is actually a doublet. This is confirmed by the Raman, luminescence, and INS spectra. The presence of two very close lying fundamentals ($T_{1u}(1)$ and $H_u(2)$) is expected from the calculations of the present work. The calculations predict two almost degenerate g-type modes in this region, and two appropriate bands are identified in the Raman spectrum by Love et al.[19] and also in the infrared spectrum of the crystal. The modes assignment below 600 cm^{-1} fully agrees with the results of inelastic neutron-scattering analysis of the eigenvectors of internal modes reported by Heid et al.[37]

The analysis of the spectrum above 1000 cm^{-1} is somehow simpler. For the assignment of the $G_g(4)$ mode, we propose the

TABLE 1: Vibrational Frequencies (cm^{-1}) of C_{60}

	calculated	assignment			
	this work	this work	Schettino et al.[7]	Choi et al.[8]	Menéndez et al.[9]
A_g	487	496	494	495	496
	1474	1468	1468	1470	1470
H_g	261	264	266	267	272
	429	430	431	431	433
	705	709	709	711	709
	772	773	772	775	772
	1104	1101	1095	1101	1099
	1251	1251	1248	1251	1252
	1426	1425	1421	1427	1425
	1585	1576	1574	1576	1575
T_{1u}	528	525	525	526	526
	577	578	578	577	575
	1189	1182	1180	1180	1182
	1431	1433	1430	1433	1429
T_{1g}	562	560	567	565	568
	823	825	860	904	831
	1276	1260	1289	1290	1289
T_{2g}	555	552	535	614	553
	724	713	764	668	756
	789	796	796	831	796
	1344	1345	1345	1340	1345
G_g	480	485	485	485	485
	565	567	577	592	567
	741	751	738	758	736
	1072	1078	1142	1040	1079
	1308	1315	1310	1348	1310
	1507	1497	1521	1497	1482
A_u	946	956	976	1078	984
T_{2u}	337	341	355	340	342
	709	706	714	716	753
	958	963	1037	955	973
	1177	1166	1190	1142	1205
	1536	1540	1566	1524	1525
G_u	351	354	345	354	353
	738	741	757	707	764
	751	756	776	797	776
	962	972	963	970	961
	1307	1307	1315	1315	1309
	1434	1428	1419	1429	1422
H_u	400	403	403	403	403
	531	533	485	535	534
	665	665	667	694	668
	729	738	738	737	743
	1219	1215	1215	1214	1223
	1343	1341	1342	1343	1344
	1576	1566	1540	1567	1567

1080 instead of the 1060 cm^{-1} as in our previous assignment since the former is present both in the infrared and Raman spectrum and in the luminescence and INS spectra as well. The calculated $T_{1u}(3)$ and $T_{1u}(4)$ modes are clearly identified in the infrared spectrum. Only one of these modes is observed in the luminescence and INS spectrum, but both are present in the Raman spectrum. The 1200−1400 cm^{-1} is not easily analyzed, particularly because there are two couples of fundamentals, [G_u(5) and G_g(5)] and [H_u(6) and T_{2g}(4)], that are almost degenerate in the DFT calculation and are observed as a doublet only in the infrared spectrum but are unresolved in the other spectra. Finally, the fundamentals occurring in the 1400−1600 cm^{-1} region (4 infrared or Raman active and 4 silent modes) are easily identified with the help of the present DFT calculations as shown in Table 1S.

As it can be seen from Tables 1 and 1S, the changes from the assignment of our previous paper[7] are not substantial and include: (a) a reassignments of the large number of fundamentals falling in the 700−800 cm^{-1} region and of the quasi-degenerate fundamentals at ∼ 950 cm^{-1}; (b) the reversal of the assignment of the couples $T_{2u}(5)$−$H_u(7)$ and $G_u(1)$−$T_{2u}(1)$ in view of the ordering of the calculated frequencies (the first reversal had already been suggested by Negri et al.[28] and confirmed by Choi et al.[8]); (c) the reassignment of the $H_u(2)$ fundamental as already suggested by Negri and by Choi, such that now the 485 cm^{-1} is not assigned twice anymore; (d) a major reassignment of $T_{2u}(3)$; (e) the reassignment of the T_{1g}(2), $T_{2g}(1)$, $G_g(2)$, $G_g(6)$, $T_{2u}(1)$, and $G_u(6)$ and a reversal of the assignment of the $G_g(5)$−$G_u(5)$ couple.

The overall agreement between calculated and observed frequencies for the present assignment is quite satisfactory. In fact, the average discrepancy is only 4.9 cm^{-1}, comparable with the misfit found for the active modes. This is a good evidence for the substantially correct choice of the experimental vibrational frequencies.

Comparing the present assignment with that proposed recently by Choi et al.,[8] the following remarks can be made. The A_u mode is calculated by Choi at 1064 cm^{-1}, a frequency considerably different from that of our calculation. As it can be seen from Table 2S, all DFT calculations predict the A_u mode at a frequency lower than 1000 cm^{-1}. The result of Choi is due to the inadequacy of the basis set adopted. In fact, we have verified that in our DFT calculation, changing from the 6-31G* to the 3-21G basis set, the A_u frequency rises by 66 cm^{-1}. The inadequacy of the procedure adopted by Choi is reflected in the resulting calculated frequency of the $T_{1g}(2)$, $T_{2g}(1)$, $T_{2g}(2)$, $T_{2g}(3)$, $G_g(2)$, $G_g(5)$, $T_{2u}(4)$, $G_u(3)$, and $H_u(3)$ normal modes. This is the basic source of the differences in the two assignments.

The assignment of the present work differs from that proposed by Menéndez and Page[9] mainly in the 700−800 cm^{-1}, where Menéndez and Page assign only one mode at the lower side of the region. Consequently, Menéndez and Page assign as fundamentals the 753 cm^{-1} peak, which is the weakest peak observed in the infrared spectrum in this region, and a shoulder of the 772 cm^{-1} peak. Our assignment is based both on the DFT calculation and on the relative infrared intensities. Another difference can be noted in the ∼ 950 cm^{-1}, where Menéndez and Page assign a fundamental at 984 cm^{-1}, but a peak at this frequency is not observed in the infrared and Raman spectra. Another difference concerns the assignment of the $T_{2u}(4)$ mode: the 1166 cm^{-1} choice should be preferred not only for the agreement with calculations but also for the much larger intensity of this peak in the infrared spectrum. This leaves a choice for the assignment of $H_u(5)$ between the 1215 and 1223 cm^{-1} peaks: we prefer the assignment at 1215 cm^{-1} on the basis of infrared intensity again. The infrared intensity criterion applies for the assignment of $T_{1g}(3)$ at 1260 cm^{-1} as well. For the assignment of $G_g(6)$, the choice should be confined to the sharp peaks at 1497 and 1505 cm^{-1} in the infrared spectrum: we prefer the former peak that is observed in the Raman spectrum as well. The same argument applies for the assignment of $T_{2u}(5)$. Of minor importance is the change of the assignment of the $G_g(5)$ mode.

Conclusions

It has been shown in this work the DFT calculations of the vibrational frequencies and intensities of fullerene C_{60} using the 6-31G* basis set are able to reproduce experiments quite accurately. The calculation are a reliable basis for the interpretation of the weaker features of the spectra and have been used to obtain a revised assignment of all the silent modes. The revised assignment has been compared with the most recent assignments reported by Choi et al.[8] and by Menéndez and Page.[9] An unknown referee suggested that the fit of the observed combination and overtone modes could be a critical test of the assignment. The huge number of predictable active binary combinations modes in the 500−3200 cm^{-1} region (151 T_{1u} and 510 $A_g + H_g$ modes) makes this rather unlikely. As a matter of fact, using the assignment obtained in this work and reported in Table 1, it is quite easy to interpret all the weak spectral features observed in addition to the assigned fundamentals in the infrared spectrum by Wang et al.[5] and Martin et al.[31] and in the Raman spectrum by Dong et al.[3]. The results are summarized in Tables S3 and S4. It is remarkable that a fit of a similar quality could be obtained by the authors[3,4,31] quoted above using an assignment of the silent modes that is considerably different from that proposed in the present paper. In fact, comparing the calculated frequencies of the silent modes obtained in the present work with the assignments deduced from the analysis of combination tones, one finds that in the cases of Dong et al.[3] and Wang et al.,[5] the average misfit is 60 cm^{-1} for the u-type and 51 cm^{-1} for the g-type modes. In the case of Martin et al.[31] the misfit is 175 cm^{-1} for the u-type and 70 cm^{-1} for the g-type modes. Considering the excellent fit found for the infrared and Raman active modes, such large discrepancies suggest that assignments based primarily on interpretations of the combination and overtone modes should be taken with some caution.

Acknowledgment. This work was supported by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST). The authors wish to thank P. Procacci for making the results of molecular dynamics simulation of crystalline C_{60} available.

Supporting Information Available: Source of the experimental frequencies of C_{60}; vibrational assignment and DFT normal modes; assignment of second-order IR and Raman modes. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press INC.: San Diego, CA, 1996.

(2) Negri, F.; Orlandi, G. *J. Phys. B* **1996**, *29*, 5049 and references therein.

(3) Dong, Z.; Zhou, P.; Holden, J. M.; Eklund, P. C. *Phys. Rev. B* **1993**, *48*, 2861.

(4) Martin, M.; Fabian, J.; Godard, J.; Bernier, P.; Lambert, J. M.; Mihaly, L. *Phys. Rev.* **1995**, *51*, 2844.

(5) Wang, K. A.; Rao, A. M.; Eklund, P. C.; Dresselhaus, M. S.; Dresselhaus, G. *Phys. Rev. B* **1993**, *48*, 11315.

(6) Giannozzi, P.; Baroni, S. *J. Chem. Phys.* **1994**, *100*, 8537.

(7) Schettino, V.; Salvi, P. R.; Bini, R.; Cardini, G. *J. Chem. Phys.* **1994**, *101*, 11079.

(8) Choi, C. H.; Kertesz, M.; Mihaly, L. *J. Phys. Chem. A* **2000**, *104*, 102.

(9) Menéndez, J.; Page, J. B. Light Scattering in Solids VIII. In *Topics in Applied Physics*; Cordona, M., Güntherodt, G., Eds.; Springer-Verlag: Berlin Heidelberg, Germany, 2000; p 27.

(10) Adams, G. B.; Page, J. B. In *Topics in Applied Physics*; Cordona, M., Güntherodt, G., Eds.; Springer-Verlag: Berlin Heidelberg, Germany, 2000; p 46.

(11) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, *99*, 3093.

(12) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(13) Schettino, V.; Gervasio, F. L.; Cardini, G.; Salvi, P. R. *J. Chem. Phys*. **1999**, *110*, 3241.

(14) Gervasio, F. L.; Cardini, G.; Salvi, P. R.; Schettino, V. *J. Phys. Chem. A* **1998**, *102*, 2131.

(15) Chelli, R.; Cardini, G.; Procacci, P.; Righini, R.; Califano, S.; Albrecht, A. *J. Chem. Phys.* **2000**, *113*, 6851.

(16) Frisch, M. J.; Trucks G. W.; Schlegel, H. B., Scuseria, G. E., Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A, Jr.; Stratmann, R. E., Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; A. D. Rabuck.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.5. Gaussian Inc.: Pittsburgh, PA, 1998.

(17) Heiney, P. A.; Fisher, J. E.; McGhie, A. R.; Romanov, W. J.; Denenstein, A. M.; McCauley, J. P.; Smith, A. B.; Cox, D. E. *Phys. Rev. Lett.* **1991**, *66*, 2911.

(18) Sachindanandam, R.; Harris, A. B. *Phys. Rev. Lett.* **1991**, *66*, 1467.

(19) Love, S. P.; McBranch, D.; Selkola, M. I.; Coppa, N. V.; Robinson, J. M.; Swanson, B. I.; Bishop, A. B. *Chem. Phys. Lett.* **1994**, *255*, 170.

(20) Cardini, G.; Bini, R.; Salvi, P. R.; Schettino, V.; Klein, M. L.; Strongin, R. M.; Brand, L.; Smith III, A. B. *J. Phys. Chem.* **1994**, *98*, 9966.

(21) Bini, R.; Procacci, P.; Salvi, P. R.; Schettino, V. *J. Phys. Chem.* **1993**, *97*, 10580.

(22) van Loosdrecht, P. H. M.; van Bentum, P. J. M.; Verheijen, M. A.; Meijer, G. *Chem. Phys. Lett.* **1992**, *198*, 587.

(23) Garrell, R. L.; Herne, T. M.; Szafranski, C. A.; Diederich, F.; Ettl, F.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 6302.

(24) Chase, B.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 2252.

(25) Cappelletti, R. L.; Copley, J. R. D.; Kamitakahara, W. A.; Li, F.; Lannin, J. S.; Ramage, D. *Phys. Rev. Lett.* **1991**, *66*, 3261.

(26) Prassides, K.; Tennis, T. J. S.; Hare, J. P.; Tomkinson, J.; Kroto, H. W.; Taylor, R.; Welton, D. R. M. *Chem. Phys. Lett.* **1991**, *187*, 455.

(27) Coulombeau, C.; Jobic, H.; Bernier, P.; Fabre, C.; Schütz, D.; Rassat, A. *J. Phys. Chem.* **1992**, *96*, 22.

(28) Negri, F.; Orlandi, G.; Zerbetto, F. *J. Phys. Chem.* **1996**, *100*, 10849.

(29) Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J.; Golden, W. G.; Seki, H.; Brown, C. A.; de Vries, M. S. *Chem. Phys. Lett.* **1991**, *179*, 181.

(30) Denisov, V. N.; Mavrin, B. N.; Ruani, G.; Zamboni, R.; Taliani, C. *Sov. Phys. JETP* **1992**, *75*, 158.

(31) Martin, M.; Du, X.; Kwon, J.; Mihaly, L. *Phys. Rev. B* **1994**, 50, 173.

(32) Procacci, P.; Cardini, G.; Salvi, P. R.; Marconi, G. *Mol. Cryst. Liq. Cryst.* **1993**, *229*, 75.

(33) Procacci, P.; Berne, B. J. *J. Chem. Phys.* **1994**, *101*, 2421.

(34) Procacci, P. Private communication, 2000.

(35) Matus, M.; Kuzmany, H. *Appl. Phys. A* **1993**, *56*, 241.

(36) Nissen, M. K.; Wilson, S. M.; Thewalt, M. L. W. *Phys. Rev. Lett.* **1992**, *69*, 2423.

(37) Heid, R.; Pintshovius, L.; Godard, J. M. *Phys. Rev. B* **1997**, *56*, 5925.